

We claim:

1. A process for forming a nanoparticle composition comprising:
 - a. polymerizing conjugated diene monomer in a hydrocarbon solvent
 - 5 to form a first reaction mixture;
 - b. charging to said reaction mixture alkenylbenzene monomer in excess of said conjugated diene monomer and catalyst to form mono-block and diblock polymers;
 - 10 c. forming micelles of said mono-block and diblock polymers; and
 - d. adding at least one crosslinking agent to cross-link said micelles and form nanoparticles, said nanoparticles having a poly(alkenylbenzene) core and an outer layer including monomer units selected from the group consisting of conjugated dienes, alkenylbenzenes, alkylanes, and mixtures thereof; and
- 15 wherein said nanoparticles have a size distribution of between about 1 and 1000 nm.
2. The process of claim 1 wherein a ratio of conjugated diene monomer to alkenylbenzene monomer is between about 0.1:1 and 0.8:1.
- 20 3. The process of claim 1 wherein said size distribution is bimodal.
4. The process of claim 1 wherein said core includes cross-linked and non-cross-linked areas.

5. The process of claim 1 wherein said size distribution is trimodal.

6. The process of claim 1 further comprising a hydrogenation step.

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7. The process of claim 1 wherein said step a is performed in the presence of a functionalized initiator.

8. The process of claim 1 wherein said alkenylbenzene monomer units are selected from the group consisting of styrene, α -methylstyrene, 1-vinyl naphthalene, 2-vinyl naphthalene, 1- α -methyl vinyl naphthalene, 2- α -methyl vinyl naphthalene, vinyl toluene, methoxystyrene, t-butoxystyrene, and the like, as well as alkyl, cycloalkyl, aryl, alkaryl, and aralkyl derivatives thereof, in which the total number of carbon atoms in the combined hydrocarbon is not greater than 18, as well as any di- or tri-vinyl substituted aromatic hydrocarbons, and mixtures thereof.

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9. The process of claim 1 wherein said conjugated diene monomer units are selected from the group consisting of 1,3-butadiene, isoprene, 1,3-pentadiene and mixtures thereof.

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10. A polymer nanoparticle composition comprising nanoparticles with a size distribution between about 1 nm and 1000 nm, and a polydispersity index between about greater than 1.15 and 8.0, wherein said nanoparticles include:

a. an outer layer including first monomer units selected from the group consisting of alkenylbenzenes, conjugated dienes, alkynes, and mixtures thereof, and

b. an inner layer including second monomer units comprised of an alkenyl, wherein said nanoparticles are comprised of more of said second monomer units than said first monomer units, and include mono-block and diblock polymer chains.

11. The composition of claim 10 wherein said size distribution is bimodal.

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12. The composition of claim 10 wherein said size distribution is trimodal.

13. The composition of claim 10 wherein the alkenylbenzene monomer units of the outer layer and the alkenylbenzene monomer units of the inner layer are independently selected from the group consisting of styrene, α -methylstyrene, 1-vinyl naphthalene, 2-vinyl naphthalene, 1- α -methyl vinyl naphthalene, 2- α -methyl vinyl naphthalene, vinyl toluene, methoxystyrene, t-butoxystyrene, and the like, as well as alkyl, cycloalkyl, aryl, alkaryl, and aralkyl derivatives thereof, in which the total number of carbon atoms in the combined hydrocarbon is not greater than 18, as well as any di- or tri-vinyl substituted aromatic hydrocarbons, and mixtures thereof.

14. The composition of claim 10 wherein said conjugated diene monomer units are selected from the group consisting of C₄-C₈ conjugated diene monomers and mixtures thereof.

5 15. The composition of claim 10, wherein said conjugated diene monomers are selected from the group consisting of 1,3-butadiene, isoprene, 1,3-pentadiene and mixtures thereof.

10 16. The composition of claim 10 wherein said alkylene monomer units are obtained by hydrogenating said conjugated diene monomer units.

17. The composition of claim 10 wherein said mono-block and di-block polymer chains are crosslinked.

15 18. A rubber composition comprising:

- a. rubber; and
- b. polymer nanoparticles having a size distribution between about 1

and 1000 nm, and including:

- i. an outer layer having monomer units selected from the group consisting of conjugated dienes, alkenylbenzenes, alkylbenzenes, and mixtures thereof, and
- ii. an inner layer including alkenylbenzene monomer units.

19. The composition of claim 18 wherein said size distribution is bimodal.
20. The composition of claim 18 wherein said size distribution is trimodal.
- 5 21. The composition of claim 18 wherein said nanoparticles are crosslinked.
22. The composition of claim 18 wherein said rubber is selected from the group consisting of synthetic polyisoprene rubber, styrene-butadiene rubber (SBR), styrene-isoprene rubber, styrene-isoprene-butadiene rubber, butadiene-isoprene
10 rubber, polybutadiene, butyl rubber, neoprene, acrylonitrile-butadiene rubber (NBR), silicone rubber, the fluoroelastomers, ethylene acrylic rubber, ethylene-propylene rubber, ethylene-propylene terpolymer (EPDM), ethylene vinyl acetate copolymer, epichlorohydrin rubber, chlorinated polyethylene-propylene rubbers, chlorosulfonated polyethylene rubber, hydrogenated nitrile rubber, terafluoroethylene-propylene rubber
15 and mixtures thereof.